

PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Slip-Casting Processes.

We, MONSANTO CHEMICALS LIMITED, a British Company, of Monsanto House, 10—18 Victoria Street, London, S.W.1, do hereby declare the invention, for which we
5 pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to slip-casting processes for the manufacture of refractory articles.

The slip-casting process is a well known method for making shaped refractory articles and can be described briefly as follows. A non-settling aqueous slurry of
15 a finely-divided refractory material and a bonding agent is poured into a dry porous mould, which is usually made of plaster. The mould soaks up and absorbs water from the slurry, building up on its surface a coating of the particles of refractory material mixed with bonding agent from which water has been withdrawn, and thus forming a
20 layer of solid material of even thickness conforming to the surface of the mould. When sufficient time has elapsed since pouring to give the desired thickness of coating on the mould surface, the excess slurry is poured off and the coating (or "casting") is
30 allowed to dry. The dry casting is removed from the mould (this is easy as the casting shrinks slightly during drying), and is then fired to give it strength, which is usually provided by some chemical interaction between the particles of refractory material and the bonding agent.

In such slip-casting processes ceramic clays are widely used as the bonding agents for the refractory particles, and the initial
40 slurry thus contains a fine dispersion of clay as well as refractory material. Clays, however, suffer from the disadvantages that they need careful preparation before use and they contain sodium or other metallic residues

which impair the refractory properties of the castings.

It has now been discovered that instead of clays, silica sols can be used as the bonding agent in these slip-casting processes provided that the slurry of refractory material and colloidal silica is appropriately stabilised and its pH adjusted so that the slurry remains homogeneous on standing. Moreover, the silica in colloidal solution appears to associate itself in some unknown way with the particles of refractory material in the slurry and when such a slurry is employed in slip-casting a high proportion of the silica remains in the coating which provides the casting and is thus available for bonding the refractory material, instead of being absorbed into the porous mould with the water as would have been expected. This discovery enables the production by slip-casting processes of shaped refractory articles, in which the bonding agent is substantially pure silica.

It is not practicable to employ slurries consisting simply of aqueous silica sol and finely-divided refractory material, for there is a tendency for the refractory particles suspended in the silica sol to settle out on standing and in fact the association referred to above does not occur. If such a slurry is used in slip-casting, there is a tendency for the refractory particles to fall out of suspension and thus provide coatings which are thicker at the bottom of the mould than those accumulating at places higher up on the mould wall solely due to the absorbing action of the mould pores. Moreover, where a reservoir of slurry is maintained for pouring into the individual moulds, the slurry will tend to become unhomogeneous as the particles settle out, and the composition of the slurry used in a series of moulds will vary. The tendency for a slurry of finely-divided refractory material and silica sol to deposit

refractory material on standing can be reduced or eliminated by the incorporation of a suitable organic stabilising agent and appropriate adjustment of the pH. The stabilising agents in some way enable the kind of association which is referred to above to occur, thus altering the nature of the surface properties of the particles of refractory material and enabling them to remain in suspension.

The process of slip-casting of the present invention is therefore one in which there is used an aqueous slurry comprising a finely-divided refractory material, a silica sol and a minor amount of an organic stabilising agent, the pH value of the slurry being such that it remains homogeneous on standing.

Silica sols which are suitable for use in the compositions of the invention include those which have been obtained by the ion-exchange process from sodium silicate, or by the so-called autoclave process employing a silica gel, such as the silica sols described in British Patents Nos. 607,696, 645,703, 649,897, 654,850 and 662,423. The concentration of silica in the silica sol used is preferably from 10% to 30% by weight and about 15% is particularly suitable. The silica sols sold under the Registered Trade Mark "Syton", such as those known as "Syton C", "Syton W-20", and "Syton 2X", which contain 15%, 15% and 30% by weight of silica respectively, are particularly suitable, and the 30% sol can if required be diluted with water to provide a 15% sol for direct use.

The powdered refractory material used will, of course, not be one which is sufficiently acidic or basic to cause the silica sol to gel rapidly. Suitable refractory materials are alumina, carborundum, chromite, silica itself and silicates such as zirconium silicate and sillimanite. The particle size of the finely-divided refractory material is preferably such that it will pass through a British Standard sieve of 200 mesh to the inch.

Suitable organic stabilising agents are non-ionic and cationic surface-active agents, and gelatine. Gelatine may be used in the form of a commercial product, such as animal glue.

Suitable non-ionic surface-active agents are condensation products of an alkylene oxide (for example ethylene oxide) with an organic substance containing a large non-polar group and an active hydrogen atom, for instance condensates of ethylene oxide with fatty alcohols (such as the product sold under the name "Lubrol W"), the condensation products of ethylene oxide with alkylphenols, for instance an octylcresol (such as "Lissapol N"), and the condensation products of ethylene oxide with alkyl mercaptans, for example a dodecyl mercaptan. Another non-ionic surface-active agent

which can be used is a polyethylene glycol fatty acid ester such as that sold under the name "Nonex 99". Examples of cationic surface-active agents which can be used are the quaternary ammonium salts such as the cetylpyridinium bromide sold under the name "Fixanol C", and cetyltrimethylammonium bromide. The words "Lubrol", "Lissapol", "Nonex" and "Fixanol" are Registered Trade Marks.

The stability of the slurry containing the refractory material, silica sol and stabilising agent is greatly influenced by its pH, and where necessary the pH must be suitably adjusted, by the addition of acid, for instance, after the ingredients of the slurry have been mixed. The most suitable pH for stability varies unpredictably with the particular production batch of silica sol used but it can easily be found by simple testing. Usually with a non-ionic surface-active agent the pH which is suitable will be on the alkaline side of neutrality, but it may be found that comparatively low pH values are acceptable when the proportion of non-ionic surface-active agent present is small. Where gelatine is used as the stabilising agent, the pH value is desirably less than 7.

The proportions of silica sol to powdered refractory material and any added water used will depend in any given instance on the thickness or "viscosity" of the slurry desired. The most suitable amount of stabilising agent employed in any particular slurry will depend to some extent on the nature of the stabilising agent as well as on the other materials present, but in general up to 1% of stabilising agent is sufficient and normally it is unnecessary or undesirable to add as much as 4%. Where a non-ionic surface-active agent is employed, from 0.05% to 1% by weight of surface-active agent is usually sufficient, and where a cationic surface-active agent is used even smaller quantities are suitable. Where gelatine is used as stabilising agent, an amount corresponding to about 0.04% by weight of the slurry is usually sufficient, though more can be added if desired.

The viscosity of a slurry used in the process of the invention is not critical and can be within a wide viscosity range. It should, however, not be too low, as the casting obtained then shrinks little on drying and consequently release from the mould is not easy. On the other hand if the viscosity of the slurry used is very high, cracks tend to appear in the casting, either while the casting is being formed in the mould or when it is dried. If the viscosity of the slurry is gauged by measuring the time taken for a given volume to flow through a standard pipette and comparing it with the time taken for water to do the same, then as a general guide, where the flow time for

water is 30 seconds, a very satisfactory flow time for a slurry suitable for use in the process of the invention is from 70 to 160 seconds.

5 In some instances where non-ionic surface-active agents are used as the stabilising agents, it may be found that the viscosity of the slurry produced increases markedly on standing, although the silica sol does not
10 gel. This behaviour appears to depend to a considerable extent on the pH of the slurry. It is possible to reduce any tendency of the slurry to thicken or increase in viscosity on standing, or even reduce to
15 the desired extent the viscosity of a slurry which is already thickened, by incorporating in addition to the non-ionic surface-active agent an anionic surface-active agent, for instance an alkylaryl sulphonate (for ex-
20 ample sodium dodecyl benzene sulphonate), a salt of an alkyl hydrogen sulphate (for example sodium lauryl sulphate, sodium cetyl sulphate or one of the commercial detergents sold under the names "Teepol"
25 and "Iranopol"), and an alkyl sulphosuccinate (for example sodium dioctyl sulphosuccinate or the substance sold under the name "Alcopol O"). Of the anionic surface-active agents which may be used to reduce
30 the thickening of a slurry in which a non-ionic surface-active agent is present there is usually necessary only a small amount in proportion to the non-ionic substance. The words "Teepol", "Iranopol" and "Alcopol"
35 are Registered Trade Marks.

Thickening of a slurry which has already occurred can generally be reduced by increasing the pH of the slurry by careful addition of an alkali, for example ammonia.
40 Slurries prepared using gelatine as stabilising agent show a tendency to be more viscous with decreasing pH, and their viscosity can be controlled by adjustment of pH. The viscosity of any slurry can of course also
45 be readjusted by the incorporation of additional quantities of one or more of its ingredients.

In carrying out the slip-casting process, the time for which the slurry needs to stand in the mould before excess slurry is poured
50 off is not only dependent on the thickness of the casting required and the absorbing characteristics of the mould, but also on the viscosity of the slurry. In practice the
55 period between pouring in the slurry and pouring off excess is usually between 2 and 10 minutes.

After the slurry has been poured off it is preferable to allow the mould containing the casting to stand for a few hours at room temperature in the open, and it is then suitable to place the mould containing the casting in a drying oven maintained at a temperature below 100° C., and conveniently
60 between 50° C. and 80° C. After drying

for a suitable period the shrunk casting is removed from the mould, and can then be fired and treated by other processes to give the finished article desired. The mould is then repeatedly re-used.

The invention is illustrated by the following Examples.

EXAMPLE 1.

Comminuted zirconium silicate passing a 200 mesh British Standard sieve (3.5 kg.; the material used was that sold under the name "Zircosil D" ("Zircosil" is a Registered Trade Mark)) was added in portions with vigorous stirring to a mixture of "Syton C" (1.200 cc.; "Syton C" is a silica sol prepared by the so-called autoclave process and containing 15% by weight of SiO₂) and 30 cc. of an aqueous solution containing 50% by weight of a non-ionic surface-active agent sold under the name "Lissapol N" (a condensation product of ethylene oxide and octylcresol): 10 cc. of 1% hydrochloric acid were then added and stirring continued for a few minutes. The pH of the slurry thus prepared was 8.4. Its "viscosity" is indicated by the time taken for 50 cc. of the slurry at a temperature of 20° C. to flow from a pipette held vertically, which was 85 seconds, while the time taken for an equal volume of water to flow from the pipette under identical conditions was found to be 30 seconds.

The slurry was poured into a dry plaster mould, allowed to stand for 5 minutes, and the excess slurry was then poured off. The mould containing the casting was then air dried at room temperature for two hours and placed in an oven at 80° C. overnight. The casting, which was in the form of a basin of wall thickness $\frac{3}{16}$ inch, was easily removed from the mould and successfully fired to 900° C. to give a refractory article of satisfactory strength and surface finish.

EXAMPLE 2.

A slurry of fused alumina (175 g., passing a 200 mesh British Standard sieve), "Syton C" (80 cc.), the non-ionic surface-active agent "Lissapol N" (0.75 cc.) and 1% hydrochloric acid (6.3 cc.) was prepared in a manner similar to that described in Example 1. This slurry was poured into a bone dry plaster mould at room temperature and allowed to stand for 10 minutes. The excess slurry was then poured off and the mould and casting were air dried at room temperature and afterwards placed in an oven at 65° C. overnight. The casting, of $\frac{1}{2}$ inch thickness, was easily removed from the mould and fired to 900° C., giving a refractory article having a good surface finish and satisfactory strength.

EXAMPLE 3.

A slurry of comminuted zirconium silicate